

Laser Heated Gradient NMR Studies of Ceramic Liquids

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Chemistry and Biochemistry

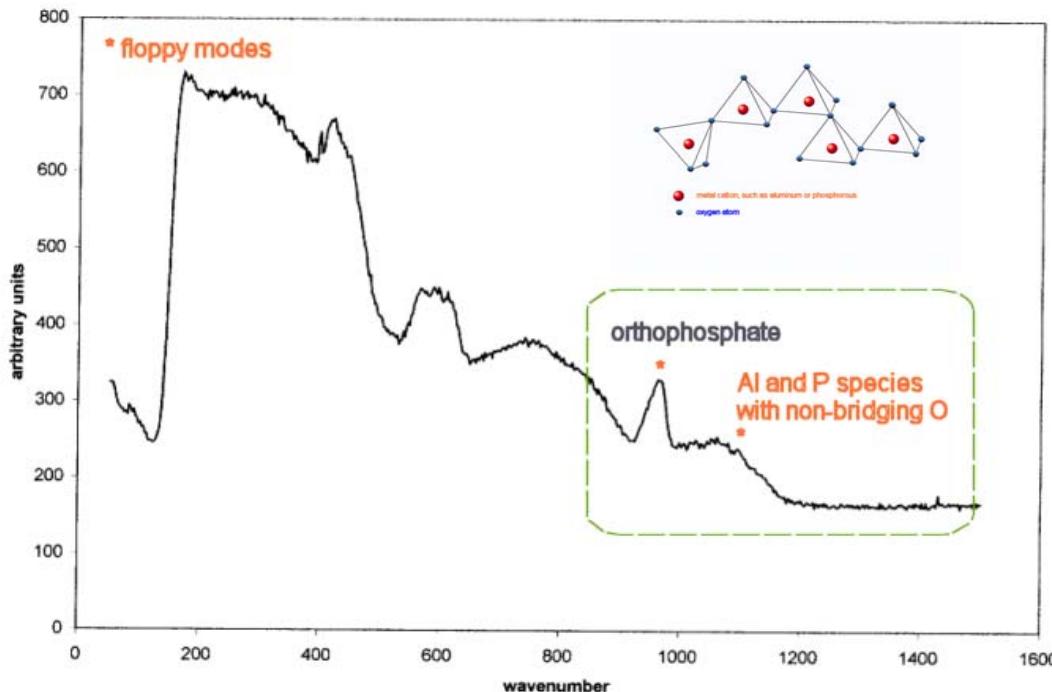
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Supported by DMR01-116361(NSF/AFOSR)

And AFOSR F4962-03-1-0346

Nanostructure of CaO-alumina-monazite melts: Raman scattering 1000-1150 wavenumbers indicates orthophosphate plus corner-linked metaphosphate AlO_4 tetrahedral chains terminated by PO_4 tetrahedra (Q_1).

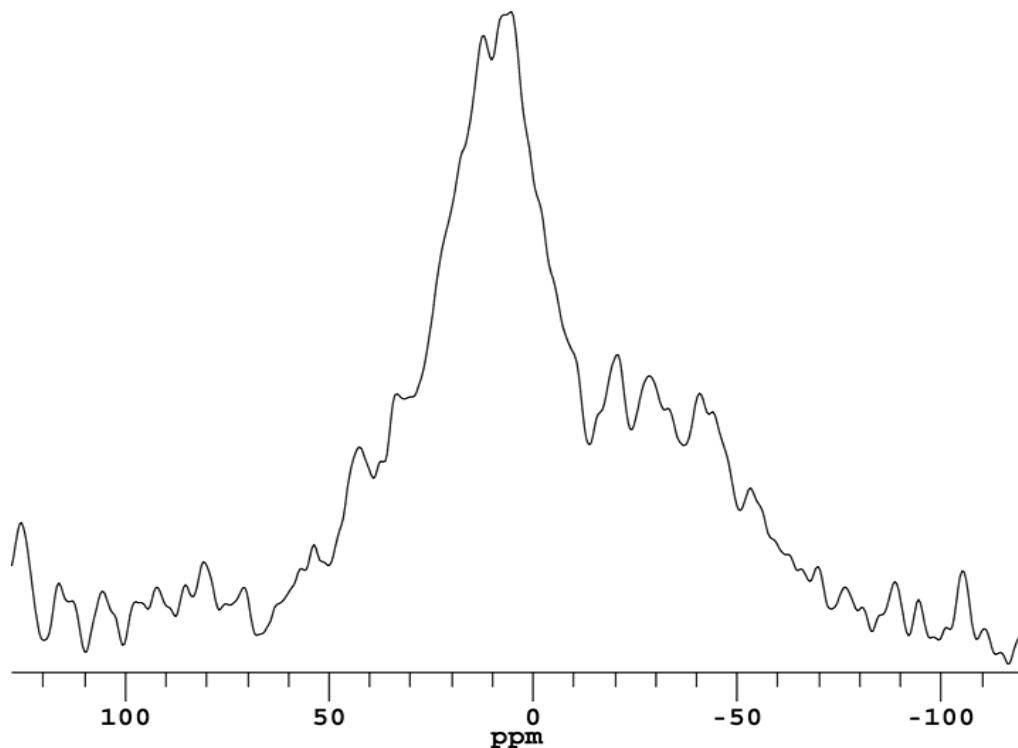
Raman Spectrum of 25% LaPO_4 in $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$



Spectrum: S. Boucher,
in Raman laboratory of
G.H. Wolf

Samples: S. Boucher
(presented at AFOSR
Contractor's meeting,
Wintergreen, VA,
August 2004)

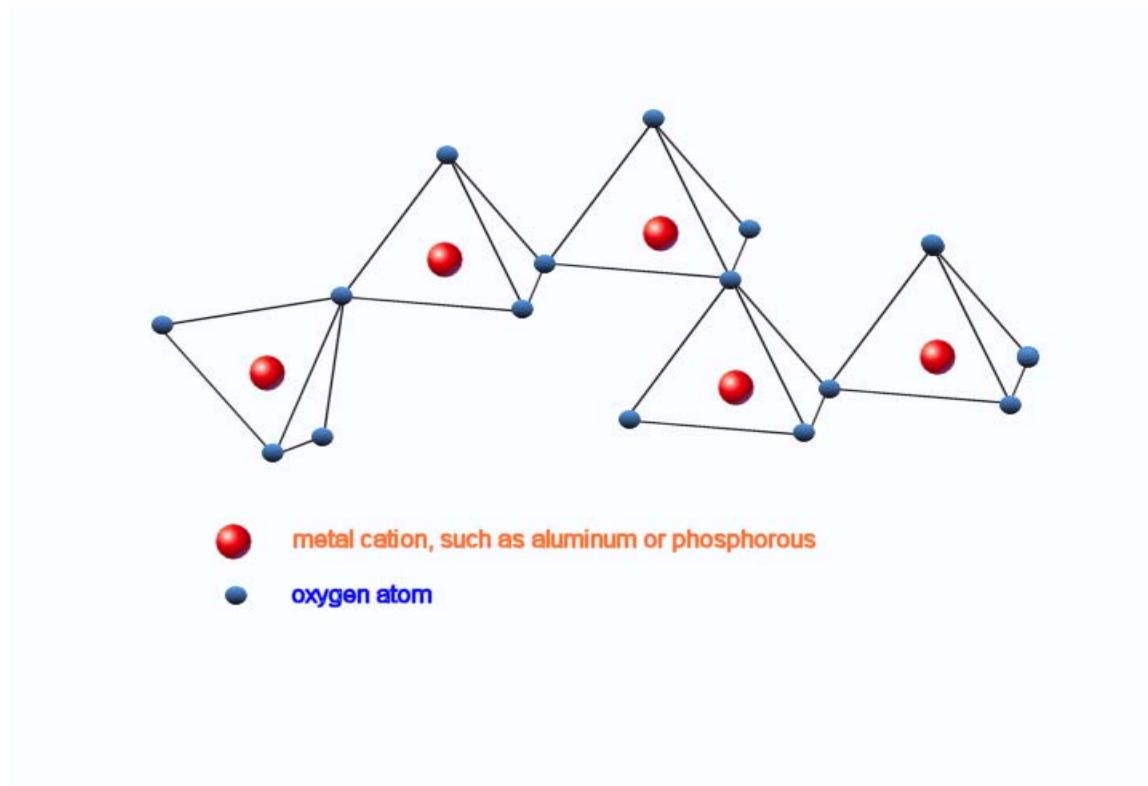
^{31}P NMR shows $\text{Q}_0\text{-}\text{Q}_1$ P-tetrahedral line (0-10 ppm shift) plus broad $\text{Q}_1\text{-}\text{Q}_3$ (~ -25 ppm) line, in 50% C_{12}A_7 :50% LaPO_4 melted and cooled to room temperature. \Rightarrow Sample composition: orthophosphate tetrahedra plus P-centered chain units ($\text{Q}_1\text{-}\text{Q}_3$), in agreement with Raman result.



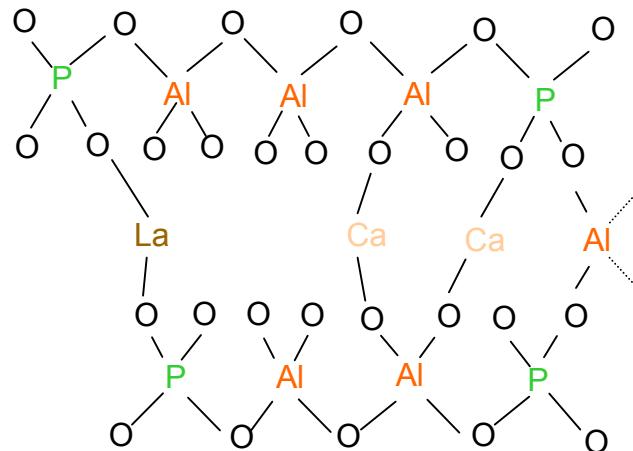
Spectrum: J.
Piwowarczyk

Samples: S.
Boucher

Model of corner-linked chain of five MO_4 tetrahedra ($\text{M} = \text{Al, P}$). Melt chains can have any length – up to 35 linked tetrahedra may be observed in phosphate glasses. Non-bridging O atoms carry charge, leading to cross-linking.

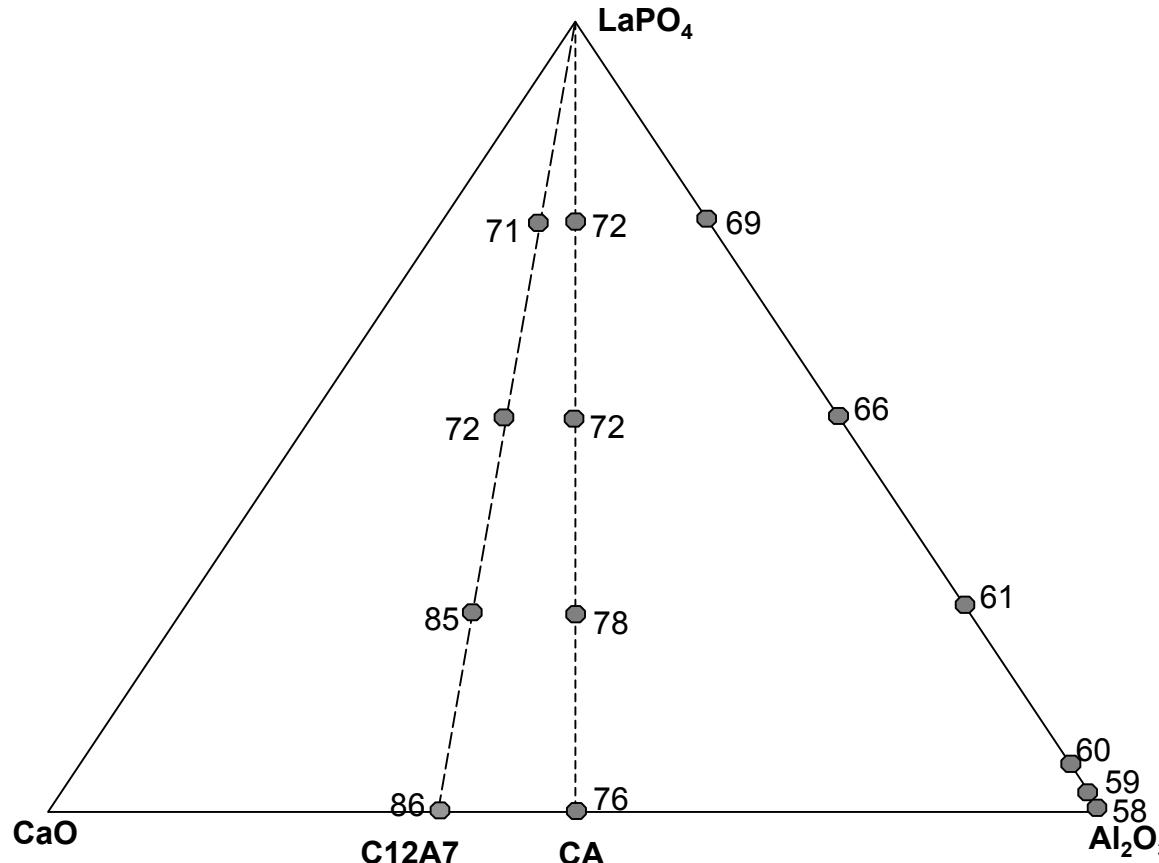


Cross linking of tetrahedral chains by metal ions:
The network former Al can also be a cross linker
(Schneider et al., 2003)



Al in crosslink position highly mobile

Composition diagram showing chemical shifts of ^{27}Al along three joins, from La monazite-rich to ceramic-rich. Strongest Al-O bonding seen for Ca^{2+} cross linking. La^{3+} cross linking weaker due to cation mass effect. (J. Europ. Ceram. Soc., accepted)



Diffusivity of Al in molten alumina measured by NMR pulsed gradient technique. Very high diffusivity values indicate possible presence of cross-linked Al in this compound. (J. Europ. Ceram. Soc., accepted.)

